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(54) **METHOD FOR PRODUCING
FLUOROALKOXIDE**

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C07C 67/29 (2006.01)
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(2013.01)

(58) **Field of Classification Search**

None
See application file for complete search history.

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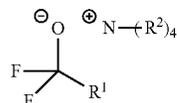
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(57) **ABSTRACT**

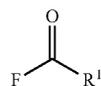
An aim of the present disclosure is to provide a method for
producing a fluoroalkoxide, said method being more useful
than conventional methods, and the like. The aim can be
achieved by a method for producing a compound repre-
sented by the following formula (1):



(wherein R¹ is a fluoroalkyl group optionally containing an
oxygen atom between carbon atoms, or a fluoroalkoxy group
optionally containing an oxygen atom between carbon
atoms, and

each R² is identical to or different from each other and is a
hydrocarbon group),

the method comprising the step of reacting
a compound represented by the following formula (2):



with a compound represented by the following formula
(3):



(56)

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**METHOD FOR PRODUCING
FLUOROALKOXIDE**

TECHNICAL FIELD

This disclosure relates to a method for producing a fluoroalkoxide.

BACKGROUND ART

Several methods are known as methods for producing fluoroalkoxide.

For example, Non-Patent Literature (NPL) 1 discloses reacting carbonyl fluoride with potassium fluoride to thereby obtain potassium perfluoromethoxide.

Patent Literature (PTL) 1 discloses reacting $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$ with trimethylamine to thereby obtain tetramethylammonium perfluoropropoxide.

Patent Literature (PTL 2) discloses reacting trifluoroacetylfluoride with tris(dimethylamino)sulfonium difluorotrimethyl silicate to thereby obtain tris(dimethylamino)sulfonium perfluoroethoxide.

CITATION LIST

Patent Literature

PTL 1: JP2016-509597A

PTL 2: U.S. Pat. No. 4,628,094

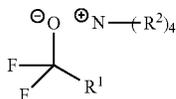
Non-Patent Literature

NPL 1: Can. J. Chem. 1965, 43, 1893

SUMMARY

The present disclosure includes the following embodiments.

A method for producing a compound represented by the following formula (1):



(wherein R^1 is a fluoroalkyl group optionally containing an oxygen atom between carbon atoms, or a fluoroalkoxy group optionally containing an oxygen atom between carbon atoms, and

each R^2 is identical to or different from each other and is a hydrocarbon group),

the method comprising the step of reacting

a compound represented by the following formula (2):



(wherein R^1 is as defined above)

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with a compound represented by the following formula (3):

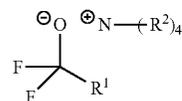


(wherein R^2 is as defined above).

The present disclosure also includes the following embodiments.

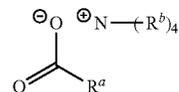
A composition comprising

a compound represented by formula (1):



(wherein R^1 is a fluoroalkyl group optionally containing an oxygen atom between carbon atoms, or a fluoroalkoxy group optionally containing an oxygen atom between carbon atoms, and each R^2 is identical to or different from each other and is a hydrocarbon group), and

a compound represented by formula (4):



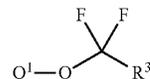
(wherein R^a is a fluoroalkyl group optionally containing an oxygen atom between carbon atoms, or a fluoroalkoxy group optionally containing an oxygen atom between carbon atoms, and

each R^b is identical to or different from each other and is a hydrocarbon group),

wherein when the sum of the content of the compound represented by formula (1) and the content of the compound represented by formula (4) is defined as 100%, the content of the compound represented by formula (1) is 70% or more in terms of molar ratio.

The present disclosure further includes the following embodiments.

A method for producing a compound represented by the following formula (5):

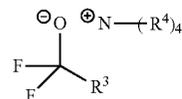


(wherein R^3 is a fluoroalkyl group optionally containing an oxygen atom between carbon atoms, or a fluoroalkoxy group optionally containing an oxygen atom between carbon atoms, and

Q^1 is an organic group),

the method comprising the step of reacting

a compound represented by the following formula (6):



(wherein R^3 is as defined above, and each R^4 is identical to or different from each other and is a hydrocarbon group)

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with a compound represented by the following formula (7):



(wherein Q^1 is as defined above and L is a leaving group).

Advantageous Effects

According to the present disclosure, a method for producing a fluoroalkoxide, the method being more useful than conventional methods, and the like are provided.

DESCRIPTION OF EMBODIMENTS

The above summary of the present disclosure is not intended to describe each disclosed embodiment or every implementation of the present disclosure.

The description of the present disclosure that follows more specifically exemplifies illustrative embodiments.

In several places throughout the present disclosure, guidance is provided through lists of examples, and these examples can be used in various combinations.

In each instance, the described list serves only as a representative group, and should not be interpreted as an exclusive list.

All of the publications, patents, and patent applications cited herein are incorporated herein by reference in their entirety.

Terms

The symbols and abbreviations in the present specification will be understood in the meaning usually used in the technical field of the present disclosure in the context of the present description, unless otherwise specified.

The term “comprising” in the present specification is used with the intention of including the meaning of the phrases “consisting essentially of” and “consisting of.”

The steps, treatments, or operations described in the present specification can be performed at room temperature, unless otherwise specified.

The room temperature referred to in the present specification can mean a temperature in the range of 10 to 40° C.

The notation “ C_{n-m} ” (wherein n and m are each a number) used in the present specification means that the number of carbon atoms is n or more and m or less, as is usually understood by persons skilled in the art.

Unless otherwise specified, examples of the “halogen” as referred to in the present specification include a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom.

The “organic group” as referred to in the present specification means a group formed by removing one hydrogen atom from an organic compound.

Examples of the “organic group” as referred to in the present specification include hydrocarbon groups optionally having one or more substituents, non-aromatic heterocyclic groups optionally having one or more substituents, heteroaryl groups optionally having one or more substituents, a cyano group, an aldehyde group, RO—, RS—, RCO—, RSO₂—, ROCO—, and ROSO₂— (wherein R is independently a hydrocarbon group optionally having one or more substituents, a non-aromatic heterocyclic group optionally having one or more substituents, or a heteroaryl group optionally having one or more substituents).

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Examples of the “substituents” include halogen atoms, a cyano group, an amino group, alkoxy groups, and alkylthio groups. Two or more substituents may be identical to or different from each other.

Unless otherwise specified, examples of “hydrocarbon groups” as referred to in the present specification include alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkadienyl, aryl, and aralkyl.

Unless otherwise specified, examples of the “alkyl” as referred to in the present specification include linear or branched C₁₋₂₀ alkyl groups, such as methyl, ethyl, propyl (n-propyl, isopropyl), butyl (n-butyl, isobutyl, sec-butyl, tert-butyl), pentyl, and hexyl.

Unless otherwise specified, examples of the “alkoxy” as referred to in the present specification include linear or branched C₁₋₂₀ alkoxy groups, such as methoxy, ethoxy, propoxy (n-propoxy, isopropoxy), butoxy (n-butoxy, isobutoxy, sec-butoxy, tert-butoxy), pentyloxy, and hexyloxy.

Unless otherwise specified, examples of the “alkylthio” as referred to in the present specification include linear or branched C₁₋₂₀ alkylthio groups, such as methylthio, ethylthio, propylthio (n-propylthio, isopropylthio), butylthio (n-butylthio, isobutylthio, sec-butylthio, tert-butylthio), pentylthio, and hexylthio.

Unless otherwise specified, examples of the “alkenyl” as referred to in the present specification include linear or branched C₂₋₂₀ alkenyl groups, such as vinyl, 1-propen-1-yl, 2-propen-1-yl, isopropenyl, 2-buten-1-yl, 4-penten-1-yl, and 5-hexen-1-yl.

Unless otherwise specified, examples of the “alkynyl” as referred to in the present specification include linear or branched C₂₋₂₀ alkynyl groups, such as ethynyl, 1-propyn-1-yl, 2-propyn-1-yl, 4-pentyn-1-yl, and 5-hexyn-1-yl.

Unless otherwise specified, examples of the “cycloalkyl” as referred to in the present specification include C₃₋₁₀ cycloalkyl groups, such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, and cycloheptyl.

Unless otherwise specified, examples of the “cycloalkenyl” as referred to in the present specification include C₃₋₁₀ cycloalkenyl groups, such as cyclopropenyl, cyclobutenyl, cyclopentenyl, cyclohexenyl, and cycloheptenyl.

Unless otherwise specified, examples of the “cycloalkadienyl” as referred to in the present specification include C₄₋₁₀ cycloalkadienyl groups, such as cyclobutadienyl, cyclopentadienyl, cyclohexadienyl, cycloheptadienyl, cyclooctadienyl, cyclononadienyl, and cyclodecadienyl.

Unless otherwise specified, the “aryl” as referred to in the present specification can be monocyclic, bicyclic, tricyclic, or tetracyclic.

Unless otherwise specified, the “aryl” as referred to in the present specification can be a C₆₋₁₈ aryl group.

Unless otherwise specified, examples of the “aryl” as referred to in the present specification include phenyl, 1-naphthyl, 2-naphthyl, 2-biphenyl, 3-biphenyl, 4-biphenyl, and 2-anthryl.

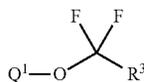
Unless otherwise specified, examples of the “aralkyl” as referred to in the present specification include benzyl, phenethyl, diphenylmethyl, 1-naphthylmethyl, 2-naphthylmethyl, 2,2-diphenylethyl, 3-phenylpropyl, 4-phenylbutyl, 5-phenylpentyl, 2-biphenylmethyl, 3-biphenylmethyl, and 4-biphenylmethyl.

Unless otherwise specified, the “non-aromatic heterocyclic group” as referred to in the present specification means a group formed by removing one hydrogen atom from a non-aromatic heterocycle.

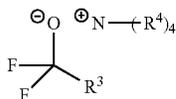
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Method for Producing Compound Represented by Formula (5)

In one embodiment, the method for producing the compound represented by the following formula (5):



(wherein R^3 is a fluoroalkyl group optionally containing an oxygen atom between carbon atoms, or a fluoroalkoxy group optionally containing an oxygen atom between carbon atoms, and Q^1 is an organic group) is a production method comprising the step of reacting a compound represented by the following formula (6):



(wherein R^3 is as defined above, and each R^4 is identical to or different from each other and is a hydrocarbon group) with a compound represented by the following formula (7):

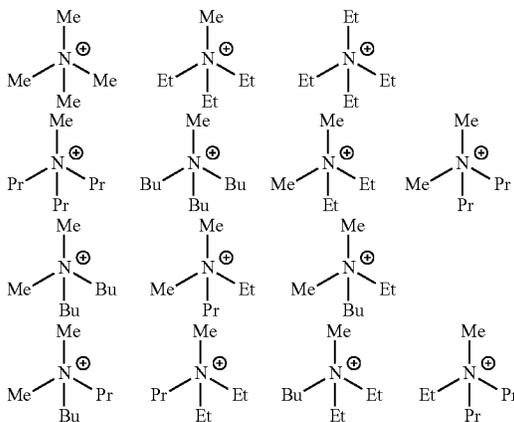


(wherein Q^1 is as defined above, and L is a leaving group).

In formulas (5) and (6), R^3 is preferably a perfluoroalkyl group optionally containing an oxygen atom between carbon atoms, or a perfluoroalkyl group optionally containing an oxygen atom between carbon atoms, more preferably a perfluoro- C_{1-8} alkyl group optionally containing an oxygen atom between carbon atoms, or a perfluoro- C_{1-8} alkoxy group optionally containing an oxygen atom between carbon atoms.

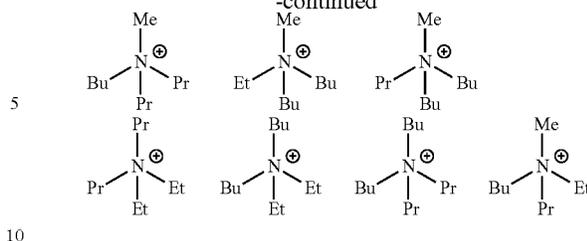
In formula (6), each R^4 is preferably alkyl, aryl, or aralkyl; more preferably alkyl; and even more preferably C_{1-4} alkyl. In view of reactivity and thermal stability, it is also preferable that all R^4 's are methyl.

A suitable example of the compound represented by formula (6) is that the anion represented by $\text{—OCF}_2\text{R}^3$ is perfluoro- C_{1-9} alkoxide and the cation represented by $\text{N(R}^4\text{)}_4$ is a compound selected from the following compounds:



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-continued



(wherein Me is methyl, Et is ethyl, Pr is propyl, and Bu is butyl).

In formula (7), Q^1 is preferably a hydrocarbon group optionally having one or more substituents; more preferably a hydrocarbon group, and even more preferably alkyl, alkenyl, aryl, or aralkyl.

Examples of leaving groups represented by L include halogen atoms (e.g., chlorine, bromine, iodine), alkylsulfonyloxy groups (e.g., mesyloxy), haloalkylsulfonyloxy groups (e.g., trifluoromethyloxy), and arylsulfonyloxy groups (e.g., tosyloxy). L is preferably a halogen atom, and is more preferably one species selected from chlorine, bromine, and iodine.

Preferable examples of the compound represented by formula (7) include alkyl halides (e.g., C_{2-20} alkyl bromides such as ethyl bromide, propyl bromide, and butyl bromide; and C_{2-20} alkyl chlorides wherein bromine of such bromides is replaced with chlorine), alkenyl halides (e.g., C_{3-20} alkenyl bromides, such as allyl bromide, 3-butenyl bromide, 4-pentenyl bromide, and 5-hexenyl bromide; and C_{3-20} alkenyl chlorides wherein bromine of such bromides is replaced with chlorine), aryl halides (e.g., C_{6-10} aryl bromides such as bromobenzene; and C_{6-10} aryl chlorides wherein bromine of such bromides is replaced with chlorine), and aralkyl halides (e.g., C_{6-10} aryl- C_{1-10} alkyl bromides such as benzyl bromide and phenethyl bromide; and C_{6-10} -aryl- C_{1-10} alkyl chlorides wherein bromine of such bromides is replaced with chlorine).

The lower limit of the amount of the compound of formula (6) to be used can usually be 0.5 mol, preferably 0.6 mol, 0.7 mol, 0.8 mol, or 0.9 mol, per mol of the compound of formula (7).

The upper limit of the amount of the compound of formula (6) to be used can usually be 10 mol, preferably 9 mol, 8 mol, 7 mol, 6 mol, or 5 mol, per mol of the compound of formula (7).

The amount of the compound of formula (6) to be used can usually be in the range of 0.5 to 10 mol, and preferably 0.9 to 5 mol, per mol of the compound of formula (7).

The reaction between the compound represented by formula (6) and the compound represented by formula (7) is preferably performed in the presence of an auxiliary agent.

Examples of the auxiliary agent include silver tetrafluoroborate, silver hexafluorophosphate, and the like. These auxiliary agents can be used alone, or in a combination of two or more.

The amount of the auxiliary agent to be used is usually in the range of 0.1 to 10 mol, and preferably 0.2 to 5 mol, per mol of the compound represented by formula (7).

The reaction between the compound represented by formula (6) and the compound represented by formula (7) is preferably performed in the presence of a solvent.

Examples of solvents include hydrocarbon solvents (e.g., chain hydrocarbons such as n-hexane; and aromatic hydrocarbons such as benzene, toluene, and p-xylene);

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halogen solvents (e.g., haloalkanes such as dichloromethane and dichloroethane; and haloarenes such as chlorobenzene);

nitrile solvents (e.g., chain nitriles such as acetonitrile, propionitrile, and acrylonitrile; and cyclic nitriles such as benzonitrile);

amide solvents (e.g., carboxylic acid amides (e.g., chain amides such as formamide, N-methylformamide, and N,N-diethylformamide; and cyclic amides such as N-methylpyrrolidone), and phosphoric acid amides (e.g., hexamethylphosphoric acid amide));

ether solvents (e.g., chain ethers such as diethyl ether; and cyclic ethers such as tetrahydrofuran, and dioxane);

urea solvents (e.g., N,N-dimethylpropylene urea);

ester solvents (e.g., esters of acetic acid);

sulfoxide solvents (e.g., dimethyl sulfoxide);

nitro solvents (e.g., nitromethane and nitrobenzene);

ketone solvents (e.g., acetone and methyl ethyl ketone);

a mixed solvent of two or more of these;

and the like.

The solvent is preferably a halogen solvent, a urea solvent, an amide solvent, a sulfoxide solvent, an ester solvent, a nitrile solvent, an ether solvent, or a mixed solvent of two or more of these, and more preferably a halogen solvent, a nitrile solvent, an amide solvent, an ether solvent, or a mixed solvent of two or more of these, and even more preferably a nitrile solvent.

In the reaction between the compound represented by formula (6) and the compound represented by formula (7), the reaction temperature and the reaction time are not particularly limited as long as the reaction proceeds. The reaction can proceed by heating.

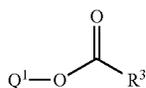
The lower limit of the reaction temperature can be, for example, 0° C., and preferably 5° C., 10° C., or 15° C.

The upper limit of the reaction temperature can be, for example, 100° C., and preferably 95° C., 90° C., 85° C., or 80° C.

The reaction temperature is, for example, in the range of 0 to 100° C., and preferably 15 to 80° C.

The reaction time is, for example, in the range of 0.5 to 24 hours, preferably 1 to 24 hours, and more preferably 1 to 18 hours.

The reaction product obtained from the compound represented by formula (6) and the compound represented by formula (7) may include, for example, a compound represented by the following formula (5'):



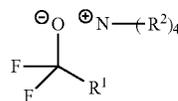
(wherein R³ and Q¹ are as defined above) as a by-product.

In the reaction product, the content (molar ratio) of the compound represented by formula (5') is, for example, 30% or less, preferably 20% or less, and more preferably 15% or less, when the total of the content of the compound represented by formula (5) and the content of the compound represented by formula (5') is defined as 100%. The content of the compound represented by formula (5') can be calculated from the ¹⁹F-NMR spectrum peak intensity. The reaction product can be purified by a conventional method, such as filtration or column chromatography.

The present disclosure includes the following embodiments.

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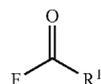
Item 1. A method for producing a compound represented by the following formula (1):



(wherein R¹ is a fluoroalkyl group optionally containing an oxygen atom between carbon atoms, or a fluoroalkoxy group optionally containing an oxygen atom between carbon atoms, and

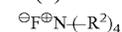
each R² is identical to or different from each other and is a hydrocarbon group),

the method comprising the step of reacting a compound represented by the following formula (2):



(wherein R¹ is as defined above)

with a compound represented by the following formula (3):



(wherein R² is as defined above).

Item 2. The method according to Item 1, wherein each R² is identical to or different from each other and is alkyl.

Item 3. The method according to Item 1 or 2, wherein each R² is identical to or different from each other and is C₁₋₄ alkyl.

Item 4. The method according to any one of Items 1 to 3, wherein all R²s are methyl.

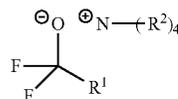
Item 5. The method according to any one of Items 1 to 4, wherein R¹ is a perfluoro-C₁₋₈ alkyl group optionally containing an oxygen atom between carbon atoms, or a perfluoro-C₁₋₈ alkoxy group optionally containing an oxygen atom between carbon atoms.

Item 6. The method according to any one of Items 1 to 5, wherein the reaction is performed in the presence of at least one solvent selected from the group consisting of halogen solvents, urea solvents, amide solvents, sulfoxide solvents, ester solvents, nitrile solvents, and ether solvents.

Item 7. The method according to any one of Items 1 to 6, wherein the reaction is performed in the presence of at least one solvent selected from the group consisting of halogen solvents, amide solvents, nitrile solvents, and ether solvents.

Item 8. The method according to any one of Items 1 to 7, wherein the reaction is performed in the presence of a nitrile solvent.

Item 9. A composition comprising a compound represented by formula (1):

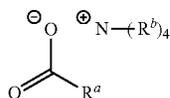


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(wherein R¹ is a fluoroalkyl group optionally containing an oxygen atom between carbon atoms, or a fluoroalkoxy group optionally containing an oxygen atom between carbon atoms, and

each R² is identical to or different from each other and is a hydrocarbon group), and

a compound represented by formula (4):



(wherein R^a is a fluoroalkyl group optionally containing an oxygen atom between carbon atoms, or a fluoroalkoxy group optionally containing an oxygen atom between carbon atoms, and

each R^b is identical to or different from each other and is a hydrocarbon group),

wherein when the sum of the content of the compound represented by formula (1) and the content of the compound represented by formula (4) is defined as 100%, the content of the compound represented by formula (1) is 70% or more in terms of molar ratio.

Item 10. The composition according to Item 9, wherein each R² is identical to or different from each other and is alkyl, and each R^b is identical to or different from each other and is alkyl.

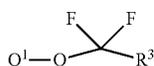
Item 11. The composition according to Item 9 or 10, wherein each R² is identical to or different from each other and is C₁₋₄ alkyl, and each R^b is identical to or different from each other and is C₁₋₄ alkyl.

Item 12. The composition according to any one of Items 9 to 11 wherein all R²s are methyl, and all R^bs are methyl.

Item 13. The composition according to any one of Items 9 to 12, wherein R¹ is a perfluoro-C₁₋₈ alkyl group optionally containing an oxygen atom between carbon atoms, or a perfluoro-C₁₋₈ alkoxy group optionally containing an oxygen atom between carbon atoms, and R^a is a perfluoro-C₁₋₈ alkyl group optionally containing an oxygen atom between carbon atoms, or a perfluoro-C₁₋₈ alkoxy group optionally containing an oxygen atom between carbon atoms.

Item 14. A fluoroalkoxylating agent comprising the composition of any one of Items 9 to 13.

Item 15. A method for producing a compound represented by the following formula (5):



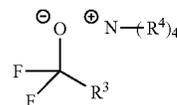
(wherein R³ is a fluoroalkyl group optionally containing an oxygen atom between carbon atoms, or a fluoroalkoxy group optionally containing an oxygen atom between carbon atoms, and

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Q¹ is an organic group),

the method comprising the step of reacting

a compound represented by the following formula (6):



(wherein R³ is as defined above, and each R⁴ is identical to or different from each other and is a hydrocarbon group)

with a compound represented by the following formula (7):



(wherein Q¹ is as defined above and L is a leaving group).

Item 16. The method according to Item 15, wherein Q¹ is a hydrocarbon group optionally having one or more substituents.

Item 17. The method according to Item 15 or 16, wherein L is a halogen atom.

Item 18. The method according to any one of Items 15 to 17, wherein each R⁴ is identical to or different from each other and is alkyl.

Item 19. The method according to any one of Items 15 to 18, wherein each R⁴ is identical to or different from each other and is C₁₋₄ alkyl.

Item 20. The method according to any one of Items 15 to 19, wherein all R⁴s are methyl.

Item 21. The method according to any one of Items 15 to 20, wherein R³ is a perfluoro-C₁₋₈ alkyl group optionally containing an oxygen atom between carbon atoms, or a perfluoro-C₁₋₈ alkoxy group optionally containing an oxygen atom between carbon atoms.

Item 22. The method according to any one of Items 15 to 21, wherein the reaction is performed at a temperature in the range of 0 to 100° C. for a period of 1 to 24 hours.

EXAMPLES

One embodiment according to the present disclosure is described below in more detail with reference to Examples. However, the present disclosure is not limited thereto or thereby.

Example 1: Synthesis of Tetramethylammonium Perfluorooctan-1-olate

In a nitrogen atmosphere, 23.8 mg of tetramethylammonium fluoride was weighed in a 10 mL pressure-resistant container, and 1 mL of acetonitrile was added.

104 mg of perfluorooctanoyl fluoride and 0.2 mL of acetonitrile were added to the container.

After stirring at room temperature for 30 minutes, the contents of the container were analyzed by ¹⁹F NMR. The analysis results indicated that the title alkoxide was obtained as a mixture with tetramethylammonium perfluoroheptanoate in a molar ratio of 87:13.

¹⁹F NMR (376 MHz, CD₃CN): δ-34.3 (br-s, 2F), -80.4 (t, J=9.7 Hz, 3F), -120.4 (t, J=13.5 Hz, 2F), -120.8 to -121.5 (m, 6F), -122.0 (m, 2F), -125.4 (n, 2F) ppm.

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Example 2: Synthesis of Tetramethylammonium Perfluorohexan-1-olate

In a nitrogen atmosphere, 23.8 mg of tetramethylammonium fluoride was weighed in a 10 mL pressure-resistant container, and 1 mL of acetonitrile was added.

79 mg of perfluorohexanoyl fluoride and 0.2 mL of acetonitrile were added to the container.

After stirring at room temperature for 30 minutes, the contents of the container were analyzed by ^{19}F NMR. The analysis results indicated that the title alkoxide was obtained as a mixture with tetramethylammonium perfluorohexanoate in a molar ratio of 88:12.

^{19}F NMR (376 MHz, CD_3CN): δ -25.5 (t, J=8.8 Hz, 2F), -80.8 (t, J=10.5 Hz, 2F), -120.6 to -120.7 (M, 2F), -121.6 (br-s, 2F), -122.3 to -122.4 (m, 2F), -125.7 (t, J=13.5 Hz, 2F) ppm.

Example 3: Synthesis of Tetramethylammonium Perfluoro-2-propoxypropan-1-olate

In a nitrogen atmosphere, 23.8 mg of tetramethylammonium fluoride was weighed in a 10 mL pressure-resistant container, and 1 mL of acetonitrile was added.

83 mg of 2-(heptafluoropropoxy)tetrafluoropropionyl fluoride and 0.2 mL of acetonitrile were added to the container.

After stirring at room temperature for 30 minutes, the content of the container was analyzed by ^{19}F NMR. The analysis results indicated that the title alkoxide was produced as a mixture with tetramethylammonium perfluoro-2-propoxypropanoate in a molar ratio of 84:16.

^{19}F NMR (376 MHz, CD_3CN): δ -29.8 (br-s, 2F), -79.7 (d, J=9.0 Hz, 3F), -81.1 (t, J=9.0 Hz, 3F), -81.7 (s, 2F), -129.5 (t, J=9.0 Hz, 2F), -137.7 (t, J=20.3 Hz, 1F) ppm.

Example 4: Synthesis of Benzyl Perfluoroethyl Ether

In a nitrogen atmosphere, 70 mg of tetramethylammonium fluoride was weighed in a 10 mL container, and 4 mL of acetonitrile was added. 325 mg of perfluoroheptaacyl fluoride and 0.8 mL of acetonitrile were added to the container.

After stirring at room temperature for 30 minutes, 35.7 μL of benzyl bromide, 70.1 mg of silver tetrafluoroborate, and 0.4 mL of acetonitrile were added.

The container was heated at 45° C. for 8 hours.

After the container was cooled to room temperature, the contents of the container were filtered through Celite using dichloromethane, and purified by silica gel column chromatography. The desired title ether was obtained with a molar yield of 52% relative to benzyl bromide.

^{19}F NMR: (376 MHz, CDCl_3): δ -80.8 (t, J=9.0 Hz, 3F), -8.47 (br-s, 2F), -121.9 (br-s, 6F), -122.7 (br-s, 2F), -125.1 (br-s, 2F), -126.2 (br-s, 2F) ppm.

Example 5: Synthesis of Allyl Perfluoroethyl Ether

In a nitrogen atmosphere, 72.6 mg of tetramethylammonium fluoride was weighed in a 10 mL container, and 2 mL of acetonitrile was added.

325 mg of perfluoroheptaacyl fluoride and 0.8 mL of acetonitrile were added.

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After stirring at room temperature for 30 minutes, 25.3 μL of allyl bromide, 70.1 mg of silver tetrafluoroborate, and 0.4 mL of acetonitrile were added.

The container was heated at 45° C. for 8 hours.

After the container was cooled to room temperature, the contents of the container were filtered through Celite using dichloromethane, and then analyzed by ^{19}F NMR. The analysis results indicated that the desired title ether was obtained with a molar yield of 38% relative to allyl bromide. ^{19}F NMR (376 MHz, CDCl_3): δ -80.6 (t, J=8.1 Hz, 3F), -84.7 (br-s, 12F), -122.0 (br-s, 2F), -122.6 (br-s, 2F), -125.0 (br-s, 2F), -126.0 (br-s, 2F) ppm.

Example 6: Synthesis of 2-(Perfluoroethoxy)ethyl Acetate

In a nitrogen atmosphere, 70 mg of tetramethylammonium fluoride was weighed in a 10 mL container, and 4 mL of acetonitrile was added.

325 mg of perfluoroheptaacyl fluoride and 0.8 mL of acetonitrile were added to the container.

After stirring at room temperature for 30 minutes, 33.2 μL of ethyl bromoacetate, 70.1 mg of silver tetrafluoroborate, and 0.4 mL of acetonitrile were added.

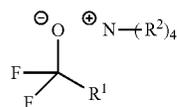
The container was heated at 45° C. for 9 hours.

After the container was cooled to room temperature, the contents of the container were filtered through Celite using dichloromethane, and then analyzed by ^{19}F NMR. The analysis results indicated that the desired title ether was obtained with a molar yield of 22% with respect to ethyl bromoacetate.

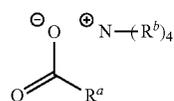
^{19}F NMR (376 MHz, CDCl_3): δ -81.5 (t, J=9.0 Hz, 3F), -85.5 (br-s, 2F), -122.3 to -122.4 (m, 6F), -123.2 (br-s, 2F), -125.6 (br-s, 2F), -126.6 (br-s, 2F) ppm.

The invention claimed is:

1. A composition comprising a compound represented by formula (1):



- wherein R^1 is a fluoroalkyl group optionally containing an oxygen atom between carbon atoms, or a fluoroalkoxy group optionally containing an oxygen atom between carbon atoms, and each R^2 is identical to or different from each other and is a hydrocarbon group, and
- a compound represented by formula (4):



- wherein R^a is a fluoroalkyl group optionally containing an oxygen atom between carbon atoms, or a fluoroalkoxy group optionally containing an oxygen atom between carbon atoms, and each R^b is identical to or different from each other and is a hydrocarbon group,

wherein R^1 is not CF_3 , C_2F_5 , or C_3F_7 , and R^a is not CF_3 , C_2F_5 , or C_3F_7 , and

wherein when the sum of the content of the compound represented by formula (1) and the content of the compound represented by formula (4) is defined as 100%, the content of the compound represented by formula (1) is 70-95% in terms of molar ratio.

2. The composition according to claim 1, wherein each R^2 is identical to or different from each other and is alkyl, and each R^b is identical to or different from each other and is alkyl.

3. The composition according to claim 1, wherein each R^2 is identical to or different from each other and is C_{1-4} alkyl, and each R^b is identical to or different from each other and is C_{1-4} alkyl.

4. The composition according to claim 1 wherein all R^2 's are methyl, and all R^b 's are methyl.

5. The composition according to claim 1, wherein R^1 is a perfluoro- C_{4-8} alkyl group optionally containing an oxygen atom between carbon atoms, or a perfluoro- C_{1-8} alkoxy group optionally containing an oxygen atom between carbon atoms, and R^a is a perfluoro- C_{4-8} alkyl group optionally containing an oxygen atom between carbon atoms, or a perfluoro- C_{1-8} alkoxy group optionally containing an oxygen atom between carbon atoms.

6. A fluoroalkoxylating agent comprising the composition of claim 1.

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